

Characterization of doping levels in heteronuclear, gas-phase, van der Waals clusters and their energy absorption from an intense optical field

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Abstract

A simple mass spectrometric method has been developed to quantify dopant levels in heteronuclear clusters in the gas phase. The method is demonstrated with reference to quantification of the water content in supersonic beams of water-doped argon clusters. Such doped clusters have assumed much importance in the context of recently-reported doping-induced enhancement in the emission of energetic charged particles and photons upon their interaction with intense laser pulses. We have also measured the energy that a doped cluster absorbs from the optical field; we find that energy absorption increases with increasing level of doping. The oft-used linear model of energy absorption is found to be quantitatively inadequate.

Key words: Clusters, supersonic beams, doping, mass spectrometry, ionization, intense laser fields

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1 Introduction

Clusters have unique properties compared with atoms, molecules and bulk matter. This is manifested most prominently in the interaction of clusters

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with intense laser fields [1,2,3]. In recent experiments, irradiation by short, intense, infrared (800 nm wavelength) laser pulses with large van der Waals clusters comprising a few thousand to several hundred thousand atoms has been extensively investigated. One of the motivations for such studies has been the unusually efficient manner in which large, gas-phase clusters absorb energy from the optical field that they are irradiated by. Energy absorption in excess of 90% has been reported for rare-gas clusters exposed to laser intensity in the range of 10^{16} W cm $^{-2}$ [4]. One consequence of this energy absorption is the ejection of a large number of electrons from the cluster. The multiply-ionized cluster subsequently undergoes Coulomb explosion, giving rise to the ejection of energetic highly-charged ions [5], electrons [6], x-ray photons [7], and the occurrence of nuclear fusion [8]. Such emissions are of obvious importance from the viewpoint of developing tabletop sources of energetic charged particles and photons. It is, therefore, not surprising that considerable effort has been expended in recent years to vary parameters like laser polarization [9], pulse width [10], and chirp [11] so as to facilitate some measure of control over the brightness and yield of the emitted charged particles and photons.

An alternative possibility of controlling cluster ionization dynamics is by *altering* not the laser parameters but the constituents of the cluster target. This approach was initially suggested by Castleman and coworkers [12] in the context of very small clusters (of size less than ~ 100 atoms); they introduced hydrogen iodide molecules into a stream of Ar gas in a supersonic jet expansion cluster source. Charge transfer processes in such few-atom clusters were postulated to lead to a change in the charge states of Ar atoms due to the presence of easily ionizable HI. It was also shown that when easily ionizable HI is present in Kr cluster expansion, higher Kr charge states were obtained [12]. Very recently, an extension of this approach has been demonstrated to control and enhance the x-ray emission from nano-cluster plasmas that are formed upon irradiation by intense femtosecond-duration laser pulses: when very large argon clusters (comprising tens of thousands of atoms) are doped with water molecules the time-integrated yield of Ar K x-ray emission has recently been shown to be enhanced nearly twelve-fold in comparison to pure Ar clusters under otherwise identical experimental conditions [13]. It appears established that by using low ionization energy dopants, it becomes possible to significantly enhance both the high-energy ion yield and the charge states that are obtained from heteronuclear clusters [14].

The doping of Ar clusters with H $_2$ O molecules (which have lower ionization energy than Ar atoms) alters the ionization dynamics of the clusters: the relative ease of ionizing the water molecules increases the number of electrons that are ionized from the cluster constituents in the initial temporal evolution of the optical pulse. This larger number of ionized electrons brings about an enhanced contribution to the optical field driven electron-impact ionization. In the laser-cluster interaction the main ionization mechanisms are (1) optical

field ionization (OFI), which includes tunnel ionization and barrier suppression ionization [1,2], (2) collisional ionization [15], and (3) charge-enhanced ionization in the combined field of ions and the laser radiation [16]. A simple OFI ionization model [2] estimate shows that the intensity threshold for H_2O is around three times lower than that for Ar. With our experimental parameters, Ar_n achieves 100% ionization when each Ar is converted into Ar^+ at an intensity of $2.5 \times 10^{14} \text{ W cm}^{-2}$ [15]. For a 100 fs FWHM Gaussian pulse with peak laser intensity of $\sim 10^{16} \text{ W cm}^{-2}$, conversion to Ar^+ occurs at time $(t-117)$ fs, where t denotes the time at which the pulse intensity peaks. The appearance intensity for a particular charge state of a given atom or ion is $\sim I_p^4$ [2], where I_p is the ionization energy of the species involved. Therefore, one electron from each water molecule will appear at an intensity of $1 \times 10^{14} \text{ W cm}^{-2}$, which occurs at time $(t-129)$ fs. Note that this time is 18 fs earlier than the time at which the first ionization of pure argon occurred. Furthermore, the enhanced ionization mechanism [17] that is so important for molecular ionization in strong fields, would lead to further increase of the ionization rate for H_2O . It is, therefore, seen that the electron density is enhanced in $(\text{Ar-H}_2\text{O})_n$ as compared to pure Ar_n . To eject the second electron from a water molecule would require another 16 eV [18,19,20]; this ionization step would occur at time $(t-114)$ fs. By the time the laser intensity reaches $\sim 2.6 \times 10^{14} \text{ W cm}^{-2}$, argon atoms are only singly ionized while water dopants are already doubly ionized. The ionized electrons may still be confined to the cluster as a whole due to Coulombic forces [21]. In the intensity regime $10^{16} \text{ W cm}^{-2}$ and for cluster sizes of more than a few nm, a substantial fraction of electrons are trapped in the potential well of the cluster [21]. Energy from the incident optical field couples to the cluster-plasma through these trapped electrons. These quasi-free electrons which are delocalized within the cluster, oscillate under the combined influence of the rapidly-increasing intra-cluster electrostatic field and the intense optical field [22], and give rise to the optical field driven electron impact ionization we referred to above. The inherent time-dependent nature of the entire process makes the temporal profile of the electron density a most critical parameter for deposition of optical energy into the cluster plasma. The consequent steeper rise in the electron density profile within the cluster thus results in enhancement of the propensity of high charge states being formed [14] as well as in significant enhancement of the yield of x-rays [13].

A most important lacuna that has plagued all recent reports on doped clusters (and the spectacular effects that doping produces in the context of irradiation by short-duration, intense optical fields) is lack of quantitative information on the level of doping that is achieved. For instance, the obvious question that arises from experiments on water-doped Ar clusters concerns quantification of the percentage of water that is present in the heteronuclear cluster. The vapor-pressure of water at room temperature is about 20 Torr. At atmospheric pressure, a typical mixture of argon-water is expected to contain about 2.6%

of water. In all hitherto-reported experiments on water-doped clusters, argon gas was bubbled through water to accomplish the doping. Therefore, on the basis of simple partial pressure arguments pertaining to a water-argon mixture, the upper limit on the percentage of water in the doped clusters cannot be more than $\sim 2.6\%$. At high values of stagnation pressure of argon, at which laser-cluster experiments are typically conducted [13,14], the proportion of water is likely to be even less than this notional limit as factors like dynamic momentum transfer and sticking coefficients make the overall situation very complex. These factors warrant a much more careful doping estimate than one that is simply based on equilibrium vapor-pressure type of arguments.

The quantification task remains challenging as a typical set-up for laser-cluster experiments would not be equipped to analyze doping levels of a few percent. We report here a relatively simple method based on mass spectrometry that helps to quantify the fraction of water in a doped heteronuclear cluster in an experimental environment that closely resembles that utilized in typical laser-cluster experiments. We demonstrate our method with reference to the amount of water dopant in an argon cluster, and we show that the enhancement in laser energy absorption increases with the doping level, in consonance with recently reported enhancements of x-ray and charged particle energies and yields under similar water-doping circumstances.

2 Experimental Method

Our experimental technique is based upon a quadrupole mass-spectrometric (QMS) analysis of species of various charge/mass values in a seeding situation of the type that pertains to doped cluster formation. A schematic view of our experimental setup is shown in Fig. 1. Argon gas jet is bubbled through triply-distilled water at various values of backing pressure. A buffer container is used to avoid spluttering of water droplets inside the experimental chamber. The Ar-water mixture is ionized by a beam of electrons of mean energy of 70 eV, with an energy spread of ~ 1 eV. The ionized gas mixture undergoes subsequent charge/mass analysis by the QMS. The background pressure of the ionization chamber is maintained at $\sim 10^{-7}$ Torr, with a typical working pressure of $\sim 10^{-6}$ Torr with full gas load. The pressure gauge head (Pfeiffer, PKR-251) to monitor vacuum in the QMS chamber and the leak valve (Pfeiffer, EVR-116) connected to the same chamber are electronically controlled through a RVC 300 controller to maintain a constant working pressure inside the experimental chamber.

In order to recreate the experimental conditions that are typical of laser-cluster interaction experiments, argon is bubbled through water at different values of backing pressures. The high-pressure argon-water mixture is then passed

through a T-tube, one port of which leaks a part of the mixed gas to the atmosphere. The leak to the atmosphere is adjusted so that a maximum of 1 bar of gas pressure is behind the leak valve into the apparatus. The mixture is then allowed to effuse into the ionization chamber in a controlled way through the RV 300 controller. As the effusion rate is inversely proportional to the square root of mass of the species, water will effuse 1.49 times faster than argon. This fact is taken into account while estimating the water content in the mixture.

The QMS generates mass spectra that allow us to determine the area under the curve of each m/q peak. Proper consideration of the ionization cross-sections of argon and water allows quantification of the proportion of each species.

For measurements of laser absorption by doped and undoped clusters, we used a supersonic, solenoid-operated Parker General Valve that was fitted with a 500 μm nozzle of 45° half expansion angle [13]. The cluster sizes were estimated using the empirical Hagen parameter [2,15]. Within the experimental parameters used in our measurements, the cluster size varies from about 350 atoms at 2 bar to about 15000 atoms at 10 bar. A Ti:Sapphire laser system that delivers up to 55 mJ (800 nm, wavelength) of 100 fs pulses at 10 Hz repetition rate was used. Laser pulses of energy up to 10 mJ/pulse were focused in the supersonic jet expansion by a 25 cm plano-convex lens to attain intensities in the $10^{15} \text{ W cm}^{-2}$ range. The scattered and transmitted 800 nm light was measured using a combination of bandpass filters and energy-calibrated, fast photodiodes placed at various locations.

It is relevant to mention that while our method is very simple, it is not expected to be as accurate as the standard gravimetric method used by gas-phase reaction kineticists [23,24]. Our primary aim is to estimate the water content in mixed Ar-water clusters. In typical laser-cluster experiments, a major source of uncertainty lies in cluster size determination. The standard Hagen method [2,15] of estimation of cluster size gives the value of mean cluster size irrespective of the distribution of cluster sizes around the mean value. (A detailed discussion of cluster size distributions has been presented elsewhere, see [25], and references therein.) The Hagen estimate has an inherent error of about 30%. With this limitation on cluster size information, the accuracy of the method we present here suffices. Moreover, the simplicity of the method enables a nearly “on-line” determination of doping levels to be made, a facet that normal gravimetric methods would not allow. We also note that mass flow controllers used in the gravimetric method usually do not work reliably in the pressure range much above 3 bar while doped cluster formation experiments usually require considerably higher pressure values.

3 Results and Discussion

Figure 2 shows the percentage of water that is present in the mixture as a function of stagnation pressure, as estimated from the QMS spectra. Particular care has been taken to get a “true” sample of the argon-water mixture: the proportion of water in the mixture is estimated as follows. At an incident electron energy of 70 eV, we take the electron impact ionization cross-section for the first ionization of neutral Ar to be 2.67 (in units of 10^{-16} cm²), while that for the second ionization is 0.146 [26]. In case of water, the respective cross-sections for ionization to H₂O⁺ and OH⁺ are 1.62 and 0.95 [27]. The inset in Fig. 2 shows a typical QMS trace when a mixture of argon and water sample was obtained upon bubbling argon through water at 5 bar backing pressure and, thereafter, being ionized by 70 eV electrons. Individual m/q species are indicated by arrows.

The proportion of water is seen to initially increase with backing pressure, starting from about 2.5% doping level at 1 bar backing pressure to a maximum of about 7% doping level at nearly 6 bar backing pressure. Thereafter, the doping level falls to about 2% at 8 bar. It is relevant to emphasize here that at backing pressure of 1 bar, the experimental measurement yields a value of 2.5% as water doping level; this value is, within the associated error bars, quite consistent with the value that is deduced using simple partial pressure arguments, as discussed in the Introduction. However, with increase of the argon backing pressure, a larger amount of argon (as density is proportional to the pressure) becomes available to “push” water molecules into forming a mixture. But, as pressure is further increased, the bulk flow velocity of argon atoms increases and, as argon gas bubbles through a finite column of water, the time that an argon atom makes contact with water reduces, as does the likelihood of momentum transfer. Consequently, there is competition between the inverse of time (\sim velocity) that argon spends in the vicinity of water and the number density of argon atoms. Beyond a certain value of pressure, in our case around 6 bar, the higher flow velocity of argon atoms becomes more important than the increment in argon atom density. Consequently, the amount of water that is carried by the swiftly flowing argon atoms is reduced. In order to reproduce the experimental conditions used in the typical doped cluster experiments [13,14], the flow conditions which include the stagnation pressure, diameter of the gas line, height of water column, etc. were kept as close to those in [13,14] as possible. For this reason alone we do not need to take into account the change in temperature of water as argon at high pressure was allowed to pass through it: our measurements do not need to make an *absolute* determination of the number of water molecules. After measurement of relative H₂O and Ar ion signals at each value of stagnation pressure we replenished the water sample and allowed sufficient time between subsequent measurements to allow for temperature equilibration.

Figure 3 shows a typical mass spectral trace when argon was directly fed into our ionization chamber, bypassing the water reservoir. This measurement provides an estimate for the background water present in the experimental chamber and gas-feed lines and provides an aid to properly estimating the actual doping level in the argon-water mixture. As can be estimated from Fig. 3, the relative yield of H_2O^+ and OH^+ is 1.1, while the ionization cross-sections would indicate this to be about 1.7. There are likely to be other sources of OH^+ in the ionization chamber, but the measured ratio is properly accounted for in all data analysis.

In order to correlate the extent of doping with the enhancements that have been recently reported in the interactions of intense, short-duration laser light with doped clusters we also carried out laser absorption measurements. Figure 4 shows some typical results of absorption measurements that we made for pure and doped Ar clusters as a function of stagnation pressure, using a fixed laser intensity of $\sim 10^{15} \text{ W cm}^{-2}$. We collected the scattered 800 nm laser light along the laser polarization, and at an angle of 90° to it, and also the transmitted light using a combination of bandpass filters and energy-calibrated, fast photodiodes placed at various locations. Given the relevant differential scattering cross-section [28,30], these measurements suffice to give a good estimate of the absorbed laser energy. Our measurements were confined to relatively low values of stagnation pressure but, nevertheless, they suffice to clearly demonstrate that absorption of laser energy is significantly more in the case of doped cluster. It is seen that within the parameter ranges of the experiments, the difference in absorption follows the trend that is indicated by the doping levels that can be quantified from data shown in Fig. 2. In the following we present a possible scenario which could explain the enhancement in the absorption of laser energy in case of doped clusters.

Clusters sizes of the type of relevance to the present study are typically a few nm, which are much smaller than the wavelength (800 nm) of the laser used in such experiments. Therefore, a cluster will experience an optical field that is uniform across its dimensions. Consequently, the typical Rayleigh type of dipole model ought to suffice in order to account for most of the observed light scattering phenomena [28] and, indeed, this is found to be the case for a large number of absorption and scattering type of laser-cluster experiments [1,2,30]. In this model, the absorption cross-section for a cluster of radius r is given by

$$\sigma_{abs} = 4\pi k r^3 \text{Im}[(\epsilon - 1)/(\epsilon + 2)], \quad (1)$$

where $k = \omega/c$ is the propagation constant of the laser (see [30], and references therein, ω is the angular frequency of the laser light and c is its speed in vacuum. ϵ is the dielectric constant of the cluster medium and is given within

the simple Drude model [15,?] by

$$\epsilon = 1 - \frac{\omega_p^2}{\omega^2} \times \frac{1}{1 + i\nu/\omega}, \quad (2)$$

where ω_p denotes the plasma frequency and ν is the electron-ion collision frequency. For a 1 keV plasma exposed to laser intensity of $\sim 10^{15}$ W cm $^{-2}$, the electron-ion collision frequency for a typical argon cluster turns out to be 0.21 fs $^{-1}$ [29], considering the typical ionic charge to be 8 and electron density in the argon cluster to be 160 nm $^{-3}$. These values are reasonable as the charge state of 8+ for Ar $_{40,000}$ clusters has been directly demonstrated by means of two-dimensional time-of-flight mass spectrometry [9,31]. Using these values, it is possible to deduce an estimate of $Im[(\epsilon - 1)/(\epsilon + 2)]$ to be 3.3×10^{-3} for homonuclear clusters of Ar atoms. Taking the percentage of water dopant in our heteronuclear clusters to be around 10%, as has been demonstrated in our data, and considering the parameters used in very recent experiments on ion ejection from doped Ar-H $_2$ O clusters [14], the estimate for $Im[(\epsilon - 1)/(\epsilon + 2)]$ turns out to be about 23% larger for water-doped clusters. However, as is clear from our experimental data, the actual enhancement of absorption between undoped and doped clusters is more than a factor of two over the entire range of stagnation pressures (cluster sizes) in our experiment. This discrepancy points to the need to develop models that will adequately take account of the fact that the optical field induces effects in clusters that are essentially nonlinear in nature. The model that is used here, and by others [1,2] takes cognizance of only linear effects.

We note that there is recent experimental evidence that doping does not entail a change in the size of the cluster [13]. The variation of the absorption with pressure that we observe is in consonance with the only earlier report [4] available in the literature.

In summary, we have presented a very simple technique to estimate the water content in water-doped argon clusters. Our technique is applicable to many other doping situations in the context of heteronuclear clusters. Doped clusters have recently assumed much importance in the light of very significant enhancement in charged particle and photon emissions that ensue upon interactions with ultrashort, intense laser pulse. The estimated percent of water dopant in the mixed clusters has also been correlated with the laser absorption measurements that we have conducted. Doped clusters absorb laser energy much more efficiently. Our results show that quantification of doping levels is possible and this will open the way for more studies on the role of low ionization energy dopants in the strong-field dynamics of laser-cluster interactions. Our energy absorption measurements show that a significant enhancement occurs when argon clusters are doped with water. It is not possible to rationalize the extent of enhancement using a linear model of the type that is reported

in the literature [1,2]. Our data brings to the fore the need to develop adequate nonlinear models that will properly account for energy absorption by the cluster from the optical field.

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Fig. 1. Experimental setup for analysis of the argon-water mixture (see text). QMS: quadrupole mass spectrometer; CEM: channel electron multiplier detector; TMP: turbomolecular pump.

Fig. 2. Percentage of water in the argon-water mixture as a function of stagnation pressure. The inset shows a typical mass spectral trace obtained when argon is bubbled through water at 5 bar backing pressure, species are indicated by arrows. The peak corresponding to the N_2^+ ion fragment is from the background nitrogen present in the experimental chamber at base pressure.

Fig. 3. A typical background mass spectral trace obtained when argon gas is directly ionized by 70 eV electrons. The peaks corresponding to various ionic fragments of water are from the background water vapor present in the chamber.

Fig. 4. Absorption of laser energy by clusters as a function of stagnation pressure for argon and doped Ar-H₂O clusters at a fixed incident laser intensity of 10^{15} W cm⁻² and wavelength of 800 nm. The data were averaged over 1000 laser shots.







